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The rotational analysis of the singlet system B of zirconium oxide. The λ 8192 band-system

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With 2 figures in the text

Abstract

A rotational analysis of the green singlet band-system B of zirconium oxide has been carried out. It has no connection with the singlet system A, as is suggested by the agreement of the vibrational constants.

The 0,0 and 1,0 bands have been analysed. Besides the main lines belonging to the molecule $Zr^{90}O^{16}$, also isotope lines ($Zr^{91}O^{16}$, $Zr^{92}O^{16}$, $Zr^{94}O^{16}$) have been identified.

The rotational constants of the main isotope are:

$$\begin{aligned} B_0'' &= 0.4167 \text{ K} \\ \alpha_{\text{cal.}} &= 0.0012 \text{ K} \\ D_0'' &= 0.35 \times 10^{-6} \text{ K} \\ B_v' &= 0.3986 - 0.0021\,(v' + \tfrac{1}{2}) \text{ K} \\ D_0' &= 0.37 \times 10^{-6} \text{ K}; \quad D_1' = 0.39 \times 10^{-6} \text{ K} \\ r_e'' &= 1.725 \times 10^{-8} \text{ cm} \\ r_e' &= 1.764 \times 10^{-8} \text{ cm.} \end{aligned}$$

System B is regarded as a $^1\Sigma$–$^1\Sigma$ or a $^1\Delta$–$^1\Delta$ transition. Its upper and lower states are called d and c respectively.

Finally, the group of ZrO bands round 8192 Å is shortly discussed.

Introduction

A considerable amount of work has been devoted to the study of the band spectrum of zirconium oxide. Thus M. Afaf has carried out a vibrational analysis in the ultraviolet, the visible and the infrared part of the spectrum [1, 2]. Rotational analyses of the strongest triplet systems α, β and γ have been made by Lagerqvist, Uhler and Barrow [3] and Uhler [4]. Moreover, a singlet system designated A ($b\,^1\Sigma$–$a\,^1\Sigma$) has been analysed rotationally by Uhler and Åkerlind [5]).

Afaf [2] has established the identity of another singlet system of ZrO. The band-head at λ 5185 Å is the 0,0 band. This system has been designated system B. The ω_e value in the upper state of system B is according to Afaf 839.2 K, and in the upper state of system A, 843.8 K. This, in his opinion, shows that the upper state of system B is $b\,^1\Sigma$. He has therefore designated this system $b\,^1\Sigma$–$c\,^1\Sigma$. If this is true, the rotational constants must also be identical. The B_0 value in the upper state $b\,^1\Sigma$ is 0.3941 (Uhler, Åkerlind [5]). From the R-branch in the 0,0 band of system B an experimental value of $\Delta B = 0.0019$ K was obtained by the writer. Thus the B_0 value in the state c should be 0.413 K, which lies in the neighhourhood of the B_0 values in the lowest triplet state $X\,^3\Delta$. It might be possible that the state c is identical with one of the substates of this term, which would not contradict the quantum rules, as $X\,^3\Delta$ probably belongs to Hund's coupling case c, because of the irregular sub-level splittings [3].

It was therefore of interest to carry out a rotational analysis of system B. The restult of this investigation is reported in this paper. The 0,0 and 1,0 bands were analysed.

Afaf [1] mentions a strong infrared band at λ 8192 Å. The rotational structure has now been measured by the present writer and the band is discussed but not analysed.

Experimental

The source of light was an arc burning between zirconium rods 3 mm in diameter. It was run at a current of 1 to 1.5 A from a 440 V D.C. supply. It was necessary to stabilize the current with a choke, as an isolating layer of oxide was formed on the rods, making it impossible to start the arc with the same rods after an interruption.

The spectrograms were taken in a first order of a Wood's 21 ft concave grating (165 000 lines in all). The dispersion in the green region is about 1.24 Å mm^{-1} and in the infrared 1.13 Å mm^{-1}. Ilford thin Film Half Tone Panchromatic Plates and sensitized Eastman Kodak I N plates were used. System B was exposed for 6 hours and the infrared system for 5 hours. Iron lines whose wave-lengths were taken from The M.I.T. Tables (1939) were used for comparison. The infrared system was photographed twice and two sets of independent measurements were made.

System *B*

The structure of the bands

The appearance of the bands is shown in Fig. 1. Every band has only one head and two branches of equal intensity, a P and an R-branch. The latter forms a conspicuous head. A considerable decrease in intensity was found in the R-branch of the 0,0 band at $\sigma = 19\,262.7$ K [$R(51)$]. Unfortunately, it was not possible to find the corresponding perturbation in the P-branch. Therefore the analysis could not be carried out with the aid of this anomaly of intensity, and was performed by finding agreeing combination differences from the 0,0 and 1,0 bands. The P-line, with its weakened intensity turned out to be masked by the 1,1 band.

In the 1,0 band the two branches were not quite so conspicuous as in the 0,0 band. No corresponding loss of intensity in the branches could be observed. The 0,1 band was weaker then the 1,0 band and was, moreover, overlapped by a comparatively strong band belonging to the γ system. It was thus not possible to perform an analysis of the 0,1 band.

The rotational structure was not fully resolved in the vicinity of the heads and no R-lines were identified before the turn of the head. The lines in the 0,0 band were picked out to $J \sim 100$ and in the 1,0 band to $J \sim 90$. Weaker lines belonging to the isotopes Zr^{91}, Zr^{92} and Zr^{94} have also been identified and are given here.

The rotational analysis

Tables 1 and 2 give the wave-numbers of the 0,0 and 1,0 bands. Lines overlapped by other band-lines or weak atomic lines are marked with an asterisk.

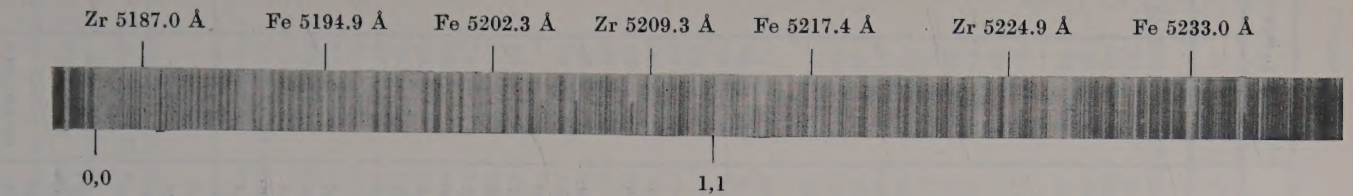

Fig. 1 a. The 0,0 band of the singlet system *B* of ZrO.

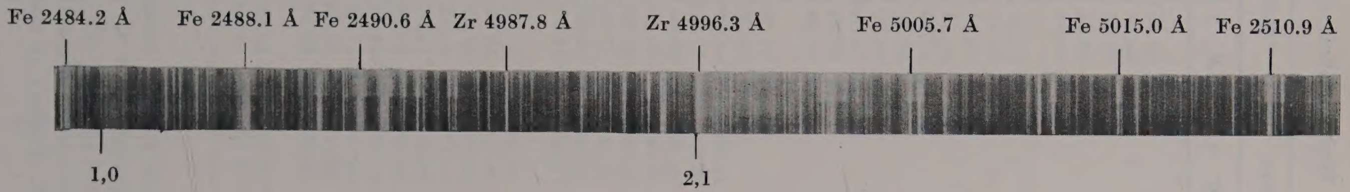

Fig. 1 b. The 1,0 band of the singlet system *B* of ZrO.

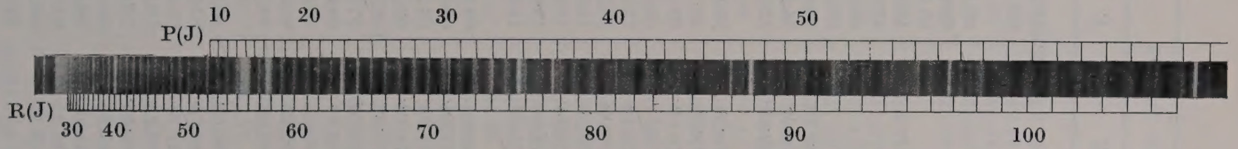

Fig. 1 c. The rotational structure of the *B* 0,0 band. The weakened *R*-line and the corresponding *P*-line are dotted.

Table 1. Wavenumbers of B 0,0.

J	$Zr^{90}O^{16}$		$Zr^{91}O^{16}$	$Zr^{92}O^{16}$		$Zr^{94}O^{16}$	
	R	P	P	R	P	R	P
18		19 251.39					19 251.67
19		50.13					50.38
20		48.44					48.71
21		46.94					47.16
22		45.38					45.80*
23		43.71*					atom
24		42.08*					42.56*
25		40.24*					40.44*
26		38.44*					38.84*
27	19 280.22	36.63*					36.98*
28	79.96	34.72*					35.06*
29	79.69	32.94					33.34*
30	79.33	30.92					31.27*
31	78.91	28.75*					29.15*
32	78.50	26.92					27.09*
33	78.01	24.83					25.02*
34	77.46	22.73*					23.01
35	76.96	20.66*					atom
36	76.37	18.49*					18.86
37	75.74	16.21*					atom
38	75.09	13.97*			19 214.20		14.55
39	74.33	11.67			11.96		12.24
40	atom	09.30			09.66		09.92
41	72.85	06.96*			07.28		07.66
42	71.99	04.61			05.00		05.21
43	71.10	02.17			02.47		02.86
44	70.27	199.70			00.03		00.28
45	69.24	97.20			197.45		197.92
46	68.31	94.61			94.94		95.26
47	67.28	92.02			92.44		92.93
48	66.25	89.41			89.78		90.09
49	65.08	86.72			87.05		87.48
50	64.01	84.00			84.44		84.85
51	62.74	81.26			81.64		82.11
52	61.54	78.50			78.81		79.18
53	60.23*	75.68			76.00		76.51
54	59.00*	72.79			73.24		73.84*
55	57.63	69.89			70.30		70.84*
56	atom	66.97			67.42		67.83*
57	54.85	63.97			64.44		64.95
58	53.37	60.95			atom		62.03
59	51.92	57.91			58.54*		59.03
60	50.38*	54.85			55.30*		55.74*
61	48.71*	51.57			52.09*		52.57*
62	47.16*	48.45			48.92		49.40
63	45.56	45.27			45.78	19 245.80*	46.10
64	43.71*	42.06	19 142.21		42.56	atom	43.03

(*continued*)

Table 1 (*continued*)

J	$Zr^{90}O^{16}$		$Zr^{91}O^{16}$	$Zr^{92}O^{16}$		$Zr^{94}O^{16}$	
	R	P	P	R	P	R	P
65	19 242.08*	19 138.73	19 138.98		19 139.32	19 242.56*	19 139.70
66	40.24*	35.35	35.66		35.92	40.44*	36.30
67	38.44*	32.04	32.27		32.57	38.84*	33.14
68	36.63*	28.58	28.84		29.12	36.98*	29.66
69	34.72*	atom	atom		25.73	35.06*	26.12
70	32.76	21.67	22.11		22.34	33.34*	22.80
71	30.74	18.12	18.40		18.77	31.27*	19.12
72	28.75*	14.55	14.87		15.20	29.15*	15.67
73	26.57	10.99	11.23		11.50	27.09*	12.07
74	24.56	07.28	07.58		07.89	25.02*	08.51
75	22.39	03.59	03.94		atom	22.73*	04.81
76	20.20	099.90	00.23		00.51	20.66*	01.48
77	18.05	96.12	096.47		096.83	18.49	097.54
78	15.71	92.32	92.68		93.06	16.21*	93.63
79	13.38	88.50	88.79		89.10	13.97*	89.80
80	11.07	84.64	85.12		85.62	11.40	86.26
81	08.66	80.68	80.99		81.51	08.98	82.44
82	06.24	76.73	77.04	19 206.48	77.66	06.96*	78.48
83	03.70	72.70	73.02	03.99	73.33	04.32	74.47
84	01.28	68.69	69.10	01.59	69.56	01.81	70.41
85	198.68	64.54	64.88	199.01	65.28	199.33	atom
86	96.09	60.48	60.82	96.45	61.30	96.73	61.94
87	93.44	56.31	56.71	atom	57.04	94.09	57.76
88	90.77	52.14	52.44	atom	53.13	91.48	53.89
89	88.03	47.84	48.21	88.51	48.68	88.84	49.51
90	85.30	43.58	44.12	85.66	44.39	87.05	45.20
91	82.49	39.28	39.64	82.83	40.45	83.25	41.00
92	79.61	34.91	35.18	79.89	35.67	80.31	36.59
93	76.71	30.52	31.02	77.12	31.38	77.51	32.15
94	73.84*	26.04	26.44	74.09	26.90	74.60	27.59
95	70.84*	21.57	22.01	71.40	22.44	71.73	23.37
96	67.83*	17.02	17.40	68.15	17.70	68.63	18.82
97	64.81*	12.47	12.71	atom	13.37	65.77	14.26
98	61.74*	07.84	08.35	62.50	08.74	62.79	09.64
99	58.54*	03.18	03.66	59.22	04.34	59.66	05.06
100	55.30*	18 998.53	99.03	55.74*	18 999.47	56.30	00.69
101	52.09*	93.71	atom	52.57*	94.54	52.99	18 995.68

On the assumption that the system B has a level in common with system A, the analysis could not be performed. It was impossible to find agreeing combination differences. As mentioned above, the analysis was carried out with the aid of combination differences from the 0,0 and 1,0 bands. The agreement of the $\Delta_2 F''(J)$ values of the main isotope is shown in Table 3. The errors seldom exceed 0.2 K.

Evaluation of the constants.—The rotational constants were determined graphically in the usual manner. The magnitude of the B and D values is the same

Table 2. Wavenumber of *B* 1,0.

J	$Zr^{40}O^{16}$		$Zr^{91}O^{16}$		$Zr^{92}O^{16}$		$Zr^{94}O^{16}$	
	R	*P*	*R*	*P*	*R*	*P*	*R*	*P*
36		20 051.23		20 050.70*		20 050.20*		20 049.06
37		48.85*		48.39*		47.79*		46.49**
38		46.49*		45.88*		45.37*		44.13**
39	20 106.27	44.13*		43.65		atom		41.91
40	05.49	41.59*		41.12		40.59*		39.33
41	04.40	39.03*		38.48		38.00		36.76
42	03.36	36.52*		35.93		35.48*		—
43	02.55	33.82*	20 102.01	33.33	20 101.47*	32.73*		31.79**
44	01.47*	31.05*	101.04	30.52	00.20*	30.05*		29.16**
45	00.20*	28.42	099.77	27.94	099.04*	27.38*		26.51**
46	099.04*	25.85	98.43	25.32	97.77*	24.75		23.71**
47	97.77*	22.94*	97.19	22.52	96.56*	22.15		20.75**
48	96.56*	20.11*	95.98	19.64	95.44*	19.10	20 094.94*	—
49	95.44*	17.36	94.94*	16.80	93.96*	16.37	93.47*	atom
50	93.96*	14.32	93.47*	13.84*	92.72	13.37	91.69	12.50**
51	92.50	11.44	91.94	10.93*	91.26	10.56	atom	09.59
52	90.89	08.46	—	07.96*	atom	07.55	88.69	06.65
53	atom	05.29	89.00	04.91	88.69	04.52	87.09	03.50
54	88.00	02.35	87.66	01.75*	87.09	01.33	85.62	00.64
55	86.40	19 999.16*	85.93	19 998.77	85.17	19 998.37	83.85	19 997.39
56	84.84	96.03*	84.30	95.63	83.49	95.23	82.43*	94.20
57	83.15	92.87	82.43*	92.54	81.83	92.25	80.84*	atom
58	81.55	89.60	80.84*	89.31	80.42	88.87	79.16*	88.02
59	79.92	86.42	79.16*	86.07	78.59	atom	77.44*	84.82
60	78.13	83.02	77.44*	82.59	atom	82.00	75.52*	81.21
61	76.30	79.49	75.52*	79.11	75.08	78.59	73.77*	77.65
62	74.30	76.11	73.77*	75.59	73.17	75.23	71.81*	74.44
63	72.37	72.74	71.81*	72.45	71.14	72.03	atom	70.96
64	70.35	69.31	atom	69.01	atom	68.57	68.13	67.51
65	68.36	65.62	67.73	65.30	67.33	64.71	66.07	63.96
66	66.35	62.22	65.77	61.62	65.02	61.24	63.84	60.43
67	64.28	58.43	63.84	58.03	63.31	57.60	62.00	56.77
68	62.18	54.77	61.61	54.23	61.18	53.81	59.89*	53.20
69	59.89*	50.95	59.35	50.56	58.86	50.21	57.64*	49.33
70	57.64*	47.28	56.93	46.79	56.45	46.55	55.47*	45.90
71	55.47*	43.47	54.94	43.00	54.41	42.64	53.09	42.14
72	52.94	39.57	52.40	39.13	51.82	38.75	50.89	38.03
73	50.70*	35.61	50.20*	35.21	49.57	34.88	48.85*	34.26
74	48.39*	31.80	47.79*	31.42	47.45	30.91	46.49*	30.26
75	45.88*	27.85	45.37*	27.65	45.00	27.23	44.13*	26.22
76	43.29*	23.88	42.82	23.28	42.33*	22.94	41.59*	22.28
77	40.84	19.52	40.59*	19.08	40.35*	18.84	39.03*	18.12
78	38.26	15.46	37.53	15.04	37.20*	14.53	36.52*	13.96
79	35.48*	11.24	34.87	10.80	34.52*	10.40	33.82*	09.65
80	32.73*	07.17	32.35	06.87	31.79*	06.47	31.05*	05.76
81	30.05*	02.80	—	02.40	29.16*	head	28.42*	01.35
82	27.38*	898.48	26.84	898.19	26.51*	897.96	25.49	897.22

(continued)

Table 2 (*continued*)

J	$\mathrm{Zr^{90}O^{16}}$		$\mathrm{Zr^{91}O^{16}}$		$\mathrm{Zr^{92}O^{16}}$		$\mathrm{Zr^{94}O^{16}}$	
	R	*P*	*R*	*P*	*R*	*P*	*R*	*P*
83	20 024.56	19 894.15	20 024.07*	19 893.86	20 023.71	19 893.60	20 022.94*	19 892.91
84	21.65*	89.84	21.38*	89.48	20.75*	89.19	20.11*	88.65
85	18.74	85.39	18.45*	85.19	17.90	84.90	17.04	84.30
86	atom	80.92	atom	80.69	14.89	80.29	13.84*	79.83
87	12.76	76.31	12.50*	76.15	11.91	75.67	10.93*	75.37
88	09.59	71.74	atom	71.51	atom	71.30	07.96*	70.89
89	06.65	67.22	06.26	66.80	05.82	66.62	04.72	66.09
90	03.50	62.53	03.25		—	62.13	01.75*	61.51
91	00.18	atom	19 999.87		19 999.16*	57.46	19 998.37	56.70
92	19 996.90	53.12	96.39		96.03*	52.72	95.23	51.78
93		48.29				47.68		47.03
94		43.28				42.62		41.99

Table 3. Combination differences ($\mathrm{Zr^{90}O^{16}}$) $v'' = 0$.

J	From 0,0	From 1,0	*J*	From 0,0	From 1,0
40	67.37	67.24	67	111.66	111.58
41	—	68.97	68	—	113.33
42	70.68	70.58	69	114.96	114.90
43	72.29	72.31	70	116.60	116.42
44	73.90	74.13	71	118.21	118,08
45	75.66	75.62	72	119.75	119.86
46	77.22	77.26	73	121.47	121.14
47	78.90	78.93	74	122.98	122.85
48	80.56	80.41	75	124.66	124.51
49	82.25	82.24	76	126.27	126.36
50	83.82	84.00	77	127.88	127.83
51	85.51	85.50	78	129.55	129.60
52	87.06	87.21	79	131.07	131.09
53	88.75	88.54	80	132.70	132.68
54	90.34	—	81	134.34	134.25
55	92.03	91.97	82	135.96	135.90
56	93.66	93.53	83	137.55	137.54
57	—	95.24	84	139.16	139.17
58	96.94	96.73	85	140.80	140.73
59	98.52	98.53	86	142.37	142.43
60	100.35	100.43	87	143.95	—
61	101.93	102.02	88	145.60	145.54
62	103.44	103.56	89	147.19	147.06
63	105.10	104.99	90	148.75	—
64	106.83	106.75	91	150.39	150.38
65	108.36	108.13	92	151.97	151.89
66	110.04	108.13	93	153.85	153.62

Table 4. Summary of the constants.

State	B_0	B_1	$D_0 \times 10^6$	$D_1 \times 10^6$	$D_e \times 10^6$ (Kratzer)	α (Pekeris)	$r_e \times 10^8$ cm
c	0.4167		0.35		0.33	0.0012	1.725
d	0.3976	0.3955	0.37	0.39	0.36	0.0017	1.764

as those hitherto known for the molecule. Afaf's vibrational constants were used to calculate the theoretical values of α (Pekeris [6]) and D (Kratzer's relation).

The values of the constants are collected in Table 4.

CALCULATION OF THE ORIGINS.—The band-origins were calculated with the formula

$$2\sigma_0 = R(J-1) + P(J) + 2(B'' - B')J^2.$$

The intercept gives

$$0,0 \quad \sigma_0 = 19\,272.5_5 \text{ K}; \qquad 1,0 \quad \sigma_0 = 20\,107.9_5 \text{ K}.$$

THE ISOTOPE EFFECT.—Zirconium has the following five stable isotopes: Zr^{90}; Zr^{91}; $Zr^{92} : Zr^{94} : Zr^{96}$ with the relative abundances 51.46:11.23:17.11:17.40:2.80 [7]. The main lines are thus due to the molecule $Zr^{90}O^{16}$. Lines arising from $Zr^{91}O^{16}$, $Zr^{92}O^{16}$ and $Zr^{94}O^{16}$ were identified in the two bands.

The vibrational shift may be written approximately

$$\Delta\sigma_v = \sigma_v^{90} - \sigma_v^i \sim (1-\varrho)\left[(v' + \tfrac{1}{2})\,\omega_e' - (v'' + \tfrac{1}{2})\omega_e''\right],$$

where $\varrho = \sqrt{\mu^{90}/\mu^i}$. For the calculation of the vibrational displacements Afaf's [2] vibrational constants were used.

The rotational isotope displacement may be obtained from the expression

$$\Delta\sigma_r = \sigma_r^{90} - \sigma_r^i \sim (1-\varrho^2)\,(\sigma - \sigma_{\text{origin}}).$$

Fig. 2 shows the observed shift in the bands. The lines correspond to the theoretical shifts obtained from $\varrho = 0.99917$ ($Zr^{91}O^{16}$), $\varrho = 0.99836$ ($Zr^{92}O^{16}$) and $\varrho = 0.99678$ ($Zr^{94}O^{16}$).

Discussion

The rotational analysis shows that Afaf's assumption, that the upper states in system *A* and system *B* are identical, is incorrect. This conclusion is supported by the perturbation of intensity found in system *B* at *R*(51). The loss of intensity in the 0,0 band has not been found in the 1,0 band. One must therefore assume that the upper level is perturbed and consequently, if Afaf's theory were correct, the corresponding lines in the 0,0 band of system A would also be perturbed. No perturbations of this kind were, however, found in system *A*.

The analysis shows also that system *B*, like system *A*, has no state in common with any of the hitherto analysed triplet sub-levels. This is not surprising, as a

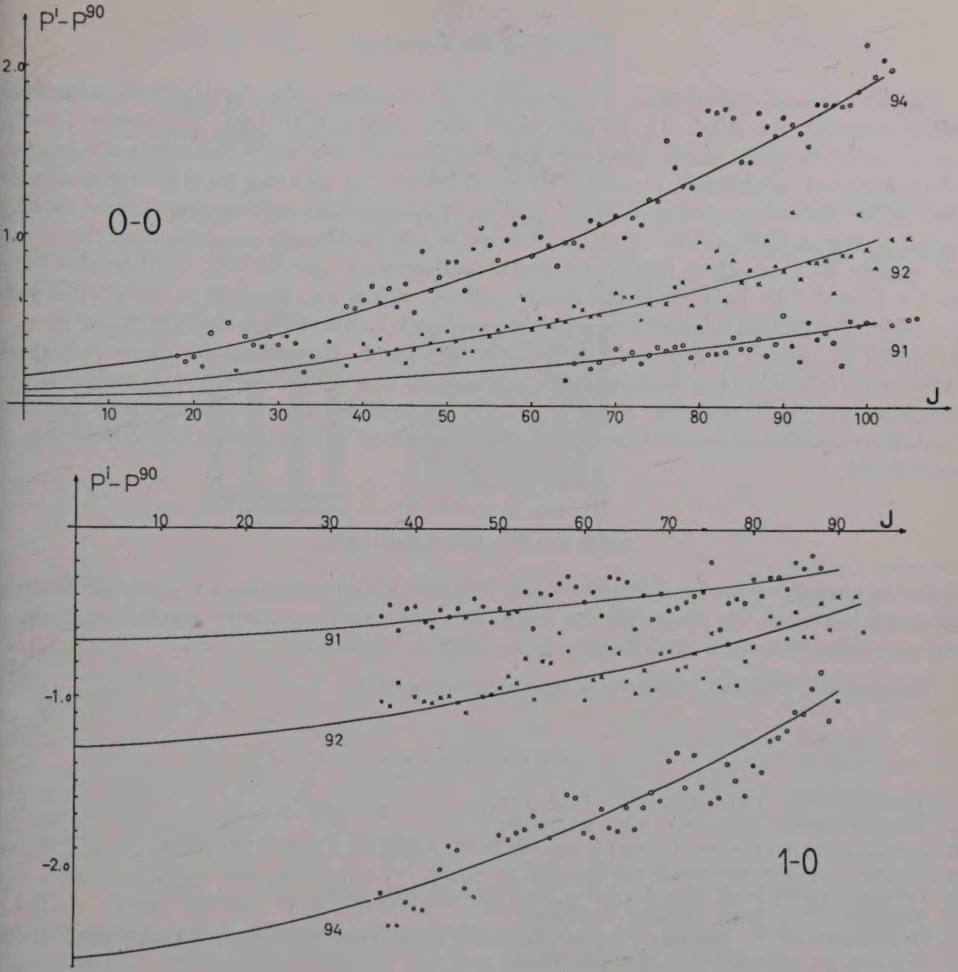

Fig. 2. Isotope effect in the 0,0 and 1,0 bands.

state common to $c\,^1\Sigma$ and $X\,^3\Delta$ would have meant that the state $a\,^1\Sigma$ would lie considerably lower than the state $X\,^3\Delta$. System *A*, like the strong triplet systems, appears in absorption in stellar spectra (Herbig [8]). One has thus reason to assume that $X\,^3\Delta$ and $a\,^1\Sigma$ do not differ very much in position.

In the absence of Λ-type doubling one may exclude the possibility that system *B* represents a $^1\Pi$–$^1\Pi$ transition. There remains the possibility that the transition is either $^1\Sigma$–$^1\Sigma$ or $^1\Delta$–$^1\Delta$, though which, it is impossible to decide at present. It is hardly likely that the molecule has four neighbouring, independent and stable $^1\Sigma$-states. If one assumes that system *A* is a $^1\Sigma$–$^1\Sigma$ transition, it is natural to regard system *B* as a $^1\Delta$–$^1\Delta$ transition. The lowest singlet term in the analogous molecule TiO is a $^1\Delta$-term. For this reason one might assume that system *A*—appearing in absorption—is a $^1\Delta$–$^1\Delta$ transition. In this case system *B* would represent a $^1\Sigma$–$^1\Sigma$ transition. The question must be left open until further information is available.

The 8192 band-system

In the infrared region there is a strong band showing a simple structure, which has been reported by Afaf [1]. It has been photographed at high dispersion by the writer and the plate shows that the band consists of two very distinct branches, an R-branch and a P-branch. It is very likely that this system has a state in common with any of the known singlet systems A and B. A rotational analysis was started on this basis. Using $\Delta_2F(J)$ values of all the known levels agreement was obtained for $v' = 1$ of system B. More than fifty combination differences agreed very well in the band at $\sigma = 12\,203.1$ K. In view of the isotope effect, which was studied in detail, the only possible vibrational assignment of this band is 1,1. There is a weaker head at $\sigma =$ 12 216.7 K, which is supposed to be the 0,0 band. However, this does not agree fully with the observed isotope effect unless the new state has an $w_e x_e$ value of the magnitude ~ 10 K. Further experimental work will be done to decide whether this tentative analysis is correct or if the coincidence of the combination differences is accidental.

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